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CONCEPT FOR A LASER INTERFERENCE ASSISTED TECHNIQUE

FOR THE SYNTHESIS OF NANOARRANGED MATERIALS

CONTENT

This text includes the following sections:

- ❑ **Summary**, with a brief description of the solution
- ❑ **Detailed Description**
- ❑ **Challenge requirements check-list** that summarizes how the solution satisfies the specific challenge requirements

SUMMARY:

This paper proposes a solution to InnoCentive's issued Challenge ·# *9933436***:**

"**ARPA-E Challenge: Macroscopic Composites with Nanoscale Order"**

The goal of this Challenge is "*find a way to make near fully dense macroscopic materials with nanoscale order. Porosity is not desirable and the presence of contaminants (such as surfactants from nanoparticle production or large amounts of binding agents) is also not desirable* ."

What is hereby proposed is a new concept, that mixes the techniques of Chemical Vapor Deposition (CVD) and Interference Lithography: nano-featured illumination pattern (obtained by laser interference) is applied on the growth substrate during a CVD fabrication process. The hypothesis is that that **the resulting "hot nano-pattern" on the substrate** associated to the light interference pattern**, will allow a geometrically selective control of the material's growth process at a nanometric scale.**

DETAILED DESCRIPTION

The suggested concept for the fabrication of nano-ordered materials **is inspired in the Interference Lithography technique to influence, at the nano-scale, the CVD growth of materials:**

Interference Lithography (extract from wikipedia):

"***Interference lithography*** *(or* ***holographic lithography****) is a technique for patterning regular arrays of fine features, without the use of complex optical systems or photomasks*

The basic principle is the same as in interferometry or holography. An interference pattern between two or more coherent light waves is set up and recorded in a recording layer (photoresist). This interference pattern consists of a periodic series of fringes representing intensity minima and maxima. Upon post-exposure photolithographic processing, a photoresist pattern corresponding to the periodic intensity pattern emerges.

For 2-beam interference, the fringe-to-fringe spacing or period is given by $(\lambda/2)/\sin(\theta/2)$, where λ is the wavelength and θ is the angle between the two interfering waves. The minimum period achievable is then half the wavelength.

By using 3-beam interference, arrays with hexagonal symmetry can be generated, while with 4 beams, arrays with rectangular symmetry are generated. Hence, by superimposing different beam combinations, different patterns are made possible.

Electron holographic lithography*:*

The technique is readily extendible to electron waves as well, as demonstrated by the practice of electron holography.[1][2] ***Spacings of a few nanometers[1] or even less than a nanometer[2] have been reported using electron waves interference****. This is because the wavelength of an electron is always shorter than for a photon of the same energy."*

Interference of shortwave light beams or electron beam (e-beam) waves results in the production of interference patterns with features in the nano or even subnano (for e-beams) scale. This phenomenon has been applied so far to directly modify surfaces at the nano level.

What is proposed now is to use the (sub)nano patterns produced by light/e-beam interference to influence the growth processes of Chemical Vapor Deposition (CVD) Techniques, based on the hypothesis that the interference pattern applied on the substrate will either hinder or promote growth in the areas where it is applied.

The interference pattern, projected on the CVD growing substrate can be considered as an "Interference Virtual Mask" for the growth process.

To understand the desired effect, a previous basic knowledge of CVD techniques is required. Again, we refer to the wikipedia as a free source of information:

Chemical vapor deposition (extract from wikipedia):

"Chemical vapor deposition (CVD) *is a chemical process used to produce high-purity, high-performance solid materials. The process is often used in the semiconductor industry to produce thin films****. In typical CVD, the wafer (substrate) is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce the desired deposit****. Frequently, volatile by-products are also produced, which are removed by gas flow through the reaction chamber.*

Microfabrication processes widely use CVD to deposit materials in various forms, including: monocrystalline, polycrystalline, amorphous, and epitaxial. These materials include: silicon, carbon fiber, carbon nanofibers, filaments, carbon nanotubes, SiO_2, silicon-germanium, tungsten, silicon carbide, silicon nitride, silicon oxynitride, titanium nitride, and various high-k dielectrics. CVD is also used to produce synthetic diamonds."

In CVD processes the volatile reagents react and/or decompose on the substrate surface to produce the desired deposit. This means that if we can locally influence (with a heat pattern) the substrate's temperature we have a means of promoting or inhibiting local growth/deposition.

The simpler conceptual array would include a CVD chamber with a cooled substrate and a laser light (or e-beam) emission and interference arrangement. Low temperature of the cooled substrate will inhibit material growth/deposition over the substrate. The light (or e-beam) interference "virtual mask" projected on the substrate will heat the substrate with a geometrical heat pattern that matches the interference pattern. Laser power will be selected so that the temperature on the substrate at the interference pattern points is enough to promote the CVD reaction/deposition/growth on the substrate.

A working design may need to include more than two or more laser being split to provide for illuminating/heating the substrate with different patterns or locations. Laser (e-beam) pulsed operation may be required, to prevent heating beyond the patterned region.

How to deposit a bicomponent material with the laser Interference + CVD technique

So far, we have exposed how the heat nano-pattern produced by Laser Interference may be suitable for growing a monocomponent material on a substrate following the nano-features of the pattern. We have two address now the problem of depositing a second material. There may be various ways to achieve this; for example:

- Using and staged (alternating) CVD method in which:
  - Stage A: using reagents and CVD conditions to deposit/grow material 1 on the substrate. Laser interference pattern 1 is applied, heating the regions where we want material 1 to be deposited/grown.
  - Stage B: using reagents and CVD conditions to deposit/grow material 2 on the substrate. Laser interference pattern 2 (that matches the voids left by pattern 1) is applied, heating the regions where we want material 2 to be deposited/grown.
  - Stages A and B are subsequently repeated to deposit alternated layers of materials 1 and 2.
  - The number of required stages may vary depending on the specific CVD technique used, materials grown and their thickness, from just two stages to

There's a very wide variety of CVD techniques and materials that can be grown with them. New techniques can be developed that may allow a rapid alternation of the conditions and reagents for the suggested "staged" CVD.

Another variant of the technique could use pulsed thermal ablation (comparable to “plain” Interference lithography) to selectively remove CVD deposited materials to create a nanopattern of materials “A” and “B”, removing material from the “unwanted areas”, in an staged CVD process with alternative depositions and partial removals of each component, following the scheme:

- **“A” material deposition**
- **Selective Ablation of material “A” using interference ablation pattern “B”**
- **“B” material deposition**
- **Selective Ablation of material “B” using interference ablation pattern “A”**
- **“A” material deposition**
- **Etc…**

NB: Further details are given in the next section, that addresses the Technical Requirements:

TECHNICAL REQUIREMENTS CHECKLIST.

1. Macroscopic*: Volume of 1 cm^3 or larger, ideally in a cubic form factor. Larger volumes are desirable. No dimension should be smaller than 0.25 cm.*

Fabrication dimensions attainable with the technique are potentially the same that CVD techniques allow. While CVD is most used for the synthesis of thin films, it is also suitable for the synthesis of much thicker materials. For example, DIDCO commercializes CVD grown diamonds in different shapes and sizes, as seen in the following resumed table:

PRODUCT	DIMENSIONS
CVD Diamond Wafers	**Diameter**: up to **120mm** **Thickness**: 0.3 – **2mm**
CVD Diamond Bars	Thickness x Width x Length 2mm x 2mm x 3-8mm

Source: DIDCO: http://www.didco.com/products/cvd.asp

The previous table shows dimensional examples of monocomponent pieces, diamond wafers and bars fabricated by CVD. Larger items exceeding the minimum required volume and dimensions can be grown for many materials.

2. Nanoscale*: Having features in at least one dimension of approximately 5 nm. Figure 1 shows examples of desired nanoscale order. Other ordered schemes (such as hexagonal packing) are also permitted.*

   The patterns/order schemes are the same that can be obtained by using two or more interfering lasers. For example those in the following image taken from Fraunhoffer IWS web:

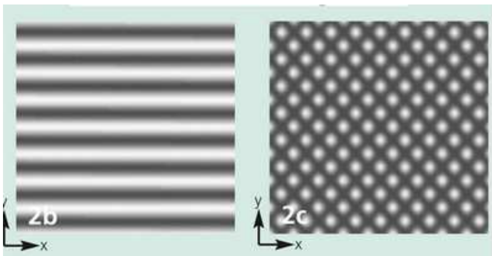

Image: examples of laser interference patterns

The Image above shows laser interference patterns. The width of the light stripes (or dots) can be as low as 1nm (*see refs. 1 and 2*). The white stripes, been areas illuminated by laser light, also correspond to “hot stripes” making up a ”thermal pattern” (called previously in this text “Interference Virtual mask”). The “dark stripes” are then colder areas. If we set up the CVD conditions so that deposition growth only occurs above (or under) the average temperature of the “cold stripes”,

As mentioned in the detailed description, Laser Interference patterns can be produced with features as small as 1 nm. While sub 1nm can be achieved with e-beam interference, the nature of e-beams limit their use to vaccum conditions, non compatible in general with CVD techniques.

Thin bicomponent films with sub 1nm features could still be possibly produced if the substrate is illuminated with the e-beam interference pattern from the back side of the CVD deposition. The back of the substrate can be maintained under vacuum conditions and thus allow the use of the e-beam interference pattern to illuminate (and locally heat) the back of the substrate. With this approach though (illumination from the back of the substrate), if feasible, the CVD bicomponent growth will be probably limited in thickness due to heat dispersion within the growing material itself, that will blur the interference virtual heat mask features as thickness increases with growth.

3. Composition: *Macroscopic materials with nanoscale order must be composed of two or more distinct components. The final macroscopic material should contain a minimum of 5% by volume of each component. Macroscopic materials with approximately equal volumes of each component are most desirable. Materials with more than two components are permitted but not required.*

On bicomponents, we partially repeat now (and expand) what was said on the detailed description:

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- *Using and staged (alternating) CVD method in which:*
    - *Stage A: using reagents and CVD conditions to deposit/grow material 1 on the substrate. Laser interference pattern 1 is applied, heating the regions where we want material 1 to be deposited/grown.*
    - *Stage B: using reagents and CVD conditions to deposit/grow material 2 on the substrate. Laser interference pattern 2 (that matches the voids left by pattern 1) is applied, heating the regions where we want material 2 to be deposited/grown.*
    - *Stages A and B are subsequently repeated to deposit alternated layers of materials 1 and 2.*
    - *The number of required stages may vary depending on the specific CVD technique used, materials grown and their thickness, from just two stages to* many.

With the proposed technique, **the percentage of each material will depend on (and can be controlled by) the power of the interfering lasers. Laser power will affect the characteristics (temperature distribution) of the resulting thermal pattern that heats the substrate**. Percentages of each component can probably be adjusted as desired from 1% to 99%, depending on the specific materials, operating conditions and the CVD technique used. For example, with a “low power” interference illumination, we can limit the hot areas that exceed the “deposition/reaction” temperature threshold to just the illuminated regions. With an high laser, the areas in which the thermal pattern is “hotter than the threshold” will extend beyond the “illuminated regions”

NOTE: The heat pattern may not be as “neat” as the black/white stripes or dots, because of heat conduction in the substrate and growing materials.

4. Materials-agnostic: *Techniques that require sophisticated linker chemistries or are only applicable to single materials are not desirable. The approach should be generalizable within families of materials (e.g. alloys, ceramics), or across different material families.*

There’s a very wide variety of CVD techniques and materials that can be grown with them. Examples of individual materials that can potentially be grown together as a nanoordered bicomponent with the proposed combined Interference+CVD technique[1] include:

- Silicon based, such as polycrystalline silicon, Silicon dioxide, Silicon nitride
- Metals and their oxides: tungsten, aluminum and copper, molybdenum, tantalum, titanium, nickel, Niobium(V) oxide, etc**2**
- Carbon based: e.g. diamond and carbon nanotubes
- Other: carbides and nitrides, Gallium arsenide, mercury cadmium telluride, etc

[1] Source: wikipedia entry on CVD, ref (4)

[2] Probably other metals such as iron can also be deposited by CVD. This has probably not done commercially for economic reasons or lack of interest.

5. Near fully dense*: Density should be >90% of the theoretical maximum. Porosity, voids, surfactants, or binding agents should be avoided as much as possible. Any materials added to the mixture to aid the formation, ordering, or alignment of the nanostructure should be removed as much as possible without leaving gaps or contaminants in the final product.*

   CVD techniques, which are the base of this proposal, produce fully dense material (see ref 3 on diamond CVD synthesis). The author sees no reasons why voids or pores would be produced with the use of the Interference + CVD combined technique to deposit two or more components

6. Stability: *After consolidation, materials must be able to maintain nanostructure up to 200 C. The ability to withstand processing temperatures of up to 300ºC or higher is preferred. Materials should also have the ability to maintain structure, order, and magnetic properties in extreme conditions, such as high magnetic fields or thermal gradients.*

   The proposal is not based in the use of binders or other extraneous materials that could affect the thermal stability of the fabricated material. Again, the post-fabrication behavior of the synthesized bi-component nano-ordered material can be compared to that of a single material obtained by current CVD techniques.

   The application of the Interference technique allows only for a thermally-mediated selective ordered deposition of each component at the nano-scale, without further influences in the resulting product.

7. Orientation/Anisotropy*: Able to control key properties (e.g. crystallinity, magnetization, or thermal conductivity) along a desired axis to induce anisotropy is desirable.*

   At this point, the author does not know if anisotropy could be induced with the proposed technique. Yet, the “geometrical” properties/characteristics of the laser light (in particular its **polarization**) used to create the “hot interference pattern” during CVD, **may** affect the electronic/magnetic properties of the material during growth **result**ing **in magnetization anisotropies in the produced material**.

Final note: the key of the proposal is the application of the nano-scale patterning/control allowed by laser interference to influence CVD material synthesis processes; whether this is best achieved through the "nanoscale thermal pattern on the substrate " generated by laser interference or more intuitively by using an alternating deposition and selective interference ablation would had to be further studied.

REFERENCES

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3. Wikipedia entry on CVD: http://en.wikipedia.org/wiki/Chemical_vapor_deposition

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